CHAPTER II

CONTROLLED MOLECULAR ALIGNMENT VIA MOLECULAR DESIGN ON AZA-METHYLENE PHENOL (1): ETHYL-4-HYDROXYBENZOATE BASED AZA-METHYLENE PHENOL COMPOUNDS

Abstract

A series of ethyl-4-hydroxybenzoate-based aza methylene phenol compounds with different hydrophobic and hydrophilic functional groups at aza and phenol groups, respectively, are reported. The preparation of each compound is structurally characterized by FTIR, ^{1}H NMR. The X-ray diffraction as well as the optical microscope technique is applied to observe the molecular alignment induced by thermal process.

Keywords: Molecular assembly, Aza-methylene phenol compounds, Molecular alignment, X-ray diffraction, Optical microscope

Introduction

Molecular assembly[1] is an asset of molecules, either individual molecule or chain of macromolecules, aligned in a regular manner via secondary forces. The secondary forces for non-covalent molecular interaction can be raised as hydrogen bonding, hydrophobic interaction, van der Waals, π-π interaction and ionic interaction. As a result, molecular assembly forms a cyclic or linear structure depending on the type of the molecules and the direction of the secondary forces in between. The conventional and informative molecular assembly in nature can be referred to DNA[2], protein[3] for cyclic type and liposomes[4], phospholipid[5] for acyclic type, where the charges, stacking conformation and hydrogen bonding play the role. For synthetic approaches, many cyclic and non-cyclic compounds have been proposed and investigated for the supramolecular structure as seen in the cases of calixarenes[6], cyclodextrin[7], crown ether[8], and phenyl propiolate[9].

The progress in analytical instruments allows us to understand the molecular assembly and the induced supramolecular specific properties. The molecular design to control the properties of materials at molecular level becomes one of the frontier technologies, so-called nano-techonology, since we can tailor-made the molecules based on various aspects of basic knowledge in chemistry.

Recently, our group clarifies the unique stereo structure and the high stability of aza-methylene phenol compounds obtained from the ring opening reaction of para-substituted phenol-based benzoxazines. The molecules are so stable that the linear polymerization is difficult to proceed[10] as well as the reaction onto the dimer unit can even be asymmetric reaction[11]. In separate work, we explored the inclusion phenomena of aza-methylene phenol compounds and its ester derivatives for metal ion responsive properties[12]. The present work is, thus, another step to challenge, by designing the aza-methylene phenol with a hydrophobic and hydrophilic group at aza and phenol ring, for molecular assembly. The molecular alignment induced from the hydrophobicity of the functional group in the molecule is expected to be a key factor for supramolecular structure compound.

Experimental

Materials. Paraformaldehyde and dodecylamine were purchased from Sigma (U.S.A.). 4-Hydroxybenzoic acid, methylamine, propylamine, and hexylamine were obtained from Fluka Chemicals (Buchs, Switzerland). 1,4-Dioxane, sodium sulfate anhydrous, and diethyl ether were purchased from Ajax Chemicals (Australia). Stearylamine were from TCI (Japan). Cyclohexylamine was from Merck (Germany). Isopropanol, sodium hydroxide, chloroform, toluene and ethanol were from Lab-Scan (Ireland). All chemicals were AR grade and used without further purification.

Measurements. Fourier transform infrared (FTIR) spectra were taken at a resolution 4 cm^{-1} by using a Bruker Equinox55/S spectrophotometer equipped with deutereted triglycine (DTGS) detector. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtained from a Bruker ACF 200 MHz spectrometer. Samples were dissolved in deuterated chloroform using 1% TMS as an internal standard. Thermal transitions were determined by using a Perkin-Elmer DSC 7 differential scanning calorimeter. Heating and cooling rate were 5°C min^{-1}. Thermogravimetric analysis was performed by a Dupont TGA 2950 analyzer. Samples were heated to 600°C with a heating rate 10°C min^{-1} under nitrogen at a flow rate 20 ml min^{-1}. Wide angle X-ray diffraction patterns were obtained from a RIGAKU RINT 2000 using CuK_α (λ = 0.145 nm) as an X-ray source and operating at 40 kV, 30 mA with Ni filter for 2θ of 5°-90° equipped with thermal adjustment.

Preparation of Ethyl-4-hydroxybenzoate. 4-Hydroxybenzoic acid (20.71 g, 150 mmol) was dissolved in toluene (500 ml). Ethanol (30ml) was added with a catalytic amount of sulfuric acid (1 ml) to the solution. The mixture was stirred and refluxed for 8 hours. The solvent was removed to obtain the white powder product. The product was recrystallized by using tetrahydrofuran (THF) to obtain **1**.

Compound **1**: 89 % yield; R_f = 0.31 (5%MeOH in $CHCl_3$); FT-IR (KBr, cm^{-1}): 3220 (br s, O-H), 1675 (s, C=O--H); ^{1}H-NMR (400MHz, $CDCl_3$, ppm): 1.36 (t, 3H, O-CH_2-*CH_3*), 4.33 (q, 2H, O-*CH_2*-CH_3), 6.88 (d, 2H, Ar-*H*), 7.97 (d, 2H, Ar-*H*).

Preparation of 3-methyl-3,4-dihydro-6-ethylformyl-2H-1,3-benzoxazine, 2, 3-propyl-3,4-dihydro-6-ethylformyl-2H-1,3-benzoxazine, 3, 3-hexyl-3,4-dihydro-6-ethylformyl-2H-1,3-benzoxazine, 4, 3-dodecyl-3,4-dihydro-6-ethylformyl-2H-1,3-benzoxazine, 5, 3-stearyl-3,4-dihydro-6-ethylformyl-2H-1,3-benzoxazine, 6, 3-cyclohexcyl-3,4-dihydro-6-ethylformyl-2H-1,3-benzoxazine, 7. Ethyl-4-hydroxybenzoate (1.66 g, 10 mmol), methylamine (0.86 ml, 10 mmol) and formaldehyde (0.60 g, 20 mmol) were dissolved in 1,4-dioxane (80 ml). The solution was stirred and refluxed for 6 hours to obtain a clear yellowish solution. After the solvent was removed, the yellowish viscous solution was obtained. The solution was dissolved in chloroform (50 ml) to extract with 3N aqueous sodium hydroxide and water. The solution was dried by sodium sulfate anhydrous. The solvent was removed to obtain the crude yellowish product. The product was further purified by vacuum distillation to obtain the viscous product **2**. Compounds **3-7** were prepared similarly by using propylamine, hexylamine, dodecylamine, stearylamine, and cyclohexylamine, respectively.

Compound **2**: 32% yield; R_f = 0.71 (5% MeOH in $CHCl_3$); FT-IR (ZnSe, cm^{-1}): 1712 (s, C=O ester), 1497 (s, C-N oxazine); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 1.34 (t, 3H, O-CH_2-*CH_3*), 2.55 (s, 3H, N-*CH_3*), 3.94 (s, 2H, Ar-*CH_2*-N), 4.29 (q, 2H, O-*CH_2*-CH_3), 4.81 (s, 2H, O-*CH_2*-N), 6.77 (d, 1H, Ar-*H*), 7.67 (s, 1H, Ar-*H*), 7.79 (d, 1H, Ar-*H*)

Compound **3**: 79% yield; R_f = 0.76 (5% MeOH in $CHCl_3$); FT-IR (ZnSe, cm^{-1}): 1711 (s, C=O ester), 1497 (s, C-N oxazine); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 0.86 (t, 3H,CH_2-*CH_3*), 1.42 (t, 3H, O-CH_2-*CH_3*), 1.55 (m, 2H, CH_2-*CH_2*-CH_3), 2.65 (t, 2H, N-*CH_2*), 3.98 (s, 2H, Ar-*CH_2*-N), 4.29 (q, 2H, O-*CH_2*-CH_3), 4.98 (s, 2H, O-*CH_2*-N), 6.74 (d, 1H, Ar-*H*), 7.66 (s, 1H, Ar-*H*), 7.84 (d, 1H, Ar-*H*)

Compound **4**: 85% yield; R_f = 0.60 (5% MeOH in $CHCl_3$); FT-IR (ZnSe, cm^{-1}): 1713 (s, C=O ester), 1497 (s, C-N oxazine); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 0.81 (t, 3H,CH_2-*CH_3*), 1.26 (m, 8H, CH_2-(*CH_2*)$_4$-CH_3), 1.32 (t, 3H, O-CH_2-*CH_3*), 2.65 (t, 2H, N-*CH_2*), 3.97 (s, 2H, Ar-*CH_2*-N), 4.24 (q, 2H, O-*CH_2*-CH_3), 4.87 (s, 2H, O-*CH_2*-N), 6.73 (d, 1H, Ar-*H*), 7.65 (s, 1H, Ar-*H*), 7.76 (d, 1H, Ar-*H*)

Compound **5**: 80% yield; R_f = 0.70 (5% MeOH in $CHCl_3$); FT-IR (ZnSe, cm^{-1}): 1715 (s, C=O ester), 1497 (s, C-N oxazine); ^{1}H-NMR (400 MHz, $CDCl_3$,

ppm): 0.84 (t, 3H,CH_2-*CH_3*), 1.26 (m, 8H, CH_2-(*CH_2*)$_{10}$-CH_3), 1.33 (t, 3H, O-CH_2-*CH_3*), 2.67 (t, 2H, N-*CH_2*), 3.98 (s, 2H, Ar-*CH_2*-N), 4.29 (q, 2H, O-*CH_2*-CH_3), 4.88 (s, 2H, O-*CH_2*-N), 6.74 (d, 1H, Ar-*H*), 7.66 (s, 1H, Ar-*H*), 7.78 (d, 1H, Ar-*H*)

Compound **6**: 79% yield; R_f = 0.68 (5% MeOH in $CHCl_3$); FT-IR (ZnSe, cm^{-1}): 1715 (s, C=O ester), 1497 (s, C-N oxazine); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 0.86 (t, 3H,CH_2-*CH_3*), 1.23 (m, 8H, CH_2-(*CH_2*)$_{16}$-CH_3), 1.34 (t, 3H, O-CH_2-*CH_3*), 2.66 (t, 2H, N-*CH_2*), 4.02 (s, 2H, Ar-*CH_2*-N), 4.28 (q, 2H, O-*CH_2*-CH_3), 4.92 (s, 2H, O-*CH_2*-N), 6.75 (d, 1H, Ar-*H*), 7.68 (s, 1H, Ar-*H*), 7.77 (d, 1H, Ar-*H*)

Compound **7**: 85% yield; R_f = 0.71 (5% MeOH in $CHCl_3$); FT-IR (ZnSe, cm^{-1}): 1712 (s, C=O ester), 1497 (s, C-N oxazine); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 1.32 (t, 3H, O-CH_2-*CH_3*), 1.80 (m, 6H, *CH_2*), 2.54 (m, 4H, *CH_2*), 2.70 (m, 4H, N-*CH*), 4.03(s, 2H, Ar-*CH_2*-N), 4.30 (q, 2H, O-*CH_2*-CH_3), 4.92 (s, 2H, O-*CH_2*-N), 6.78 (d, 1H, Ar-*H*), 7.69 (s, 1H, Ar-*H*), 7.84 (d, 1H, Ar-*H*)

Preparation of N,N'-bis(5-ehtylformyl-2-hydroxyl)methylamine, 8, N,N'-bis(5-ehtylformyl-2-hydroxyl)propylamine, 9, N,N'-bis(5-ehtylformyl-2-hydroxyl)hexylamine, 10, N,N'-bis(5-ehtylformyl-2-hydroxyl)dodecylamine, 11, N,N'-bis(5-ehtylformyl-2-hydroxyl)stearylamine, 12, N,N'-bis(5-ehtylformyl-2-hydroxyl)cyclohexylamine, 13. Compound **2** was used as a precursor to prepare **8** (Scheme I). Ethyl-4-hydroxybenzoate (1.35 g, 3.48 mmol) was added to **2** (0.70 g, 3.16 mmol). The mixture was stirred and heated at 60°C for 6 hours to obtain the yellowish viscous solution. The crude product was recrystallized by diethyl ether to obtain white powder product **8**. Similarly, compounds **9-13** were prepared by using compounds **3-7**.

Compound **8**: 87% yield; R_f = 0.60 (5% MeOH in $CHCl_3$); FT-IR (KBr, cm^{-1}): 3424 (br m, O-H), 1707 (s, C=O ester), 1686 (s, C=O--H), 1513 (s, C-N opened ring)

Compound **9**: 69% yield; R_f = 0.59 (5% MeOH in $CHCl_3$); FT-IR (KBr, cm^{-1}): 3223 (br m, O-H), 1709 (s, C=O ester), 1675 (s, C=O--H), 1515 (s, C-N opened ring); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 0.80 (t, 3H, CH_2-*CH_3*), 1.22 (m, 2H, *CH_2*-CH_3), 1.34 (t, 6H, O-CH_2-*CH_3*), 2.81 (t, 2H, N-*CH_2*), 4.03(s, 4H,

CH_2-N- *CH_2*), 4.30 (q, 4H, O-*CH_2*-CH_3), 6.90 (d, 2H, Ar-*H*), 7.86 (s, 2H, Ar-*H*), 7.90 (d, 2H, Ar-*H*)

Compound **10**: 65% yield; R_f = 0.0.61 (5% MeOH in $CHCl_3$); FT-IR (KBr, cm^{-1}): 3408 (br m, O-H), 1712 (s, C=O ester), 1687 (s, C=O--H), 1513 (s, C-N opened ring); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 0.79 (t, 3H, CH_2-*CH_3*), 1.19 (m, 2H, CH_2-*$(CH_2)_4$*-CH_3), 1.34 (t, 6H, O-CH_2-*CH_3*), 2.72 (t, 2H, N-*CH_2*), 3.93 (s, 4H, *CH_2*-N- *CH_2*), 4.29 (q, 4H, O-*CH_2*-CH_3), 6.71 (d, 2H, Ar-*H*), 7.78 (s, 2H, Ar-*H*), 7.81 (d, 2H, Ar-*H*)

Compound **11**: 62% yield; R_f = 0.63 (5% MeOH in $CHCl_3$); FT-IR (KBr, cm^{-1}): 3410 (br m, O-H), 1710 (s, C=O ester), 1683 (s, C=O--H), 1515 (s, C-N opened ring)

Compound **12**: 67% yield; R_f = 0.62 (5% MeOH in $CHCl_3$); FT-IR (ZnSe, cm^{-1}): 3345 (br m, O-H), 1713 (s, C=O ester), 1687 (s, C=O--H), 1514 (s, C-N opened ring)

Compound **13**: 80% yield; R_f = 0.56 (5% MeOH in $CHCl_3$); FT-IR (KBr, cm^{-1}): 3444 (br m, O-H), 1708 (s, C=O ester), 1686 (s, C=O--H), 1512 (s, C-N opened ring); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 0.81 (m, 6H, *CH_2*), 1.33 (t, 6H, O-CH_2-*CH_3*), 2.53 (m, 4H, *CH_2*), 2.69 (m, 1H, N-*CH*), 3.98 (s, 4H, *CH_2*-N- *CH_2*), 4.29 (q, 4H, O-*CH_2*-CH_3), 6.76 (d, 2H, Ar-*H*), 7.75 (s, 2H, Ar-*H*), 7.80 (d, 2H, Ar-*H*)

Results and Discussion

Structural Characterization. Our preliminary studies declare that when using phenol derivatives with reactive functional group as carboxylic acid, the side reaction occurred and obstructed the formation of oxazine ring. In the present work, 4-hydroxybenzoic acid is esterified to avoid the side reaction and maintain hydrophilicity at phenol group as the designed molecule. The esterification is achieved by using benzoic acid and ethanol. After esterification, **1** gives the C=O peak at 1675 cm^{-1} referred to the carbonyl with hydrogen bonding structure (Figure 1). Comparing to 4-hydroxybenzoic acid, the characterisitc that of broad band hydroxyl group of carboxylic acid appeared at 3000-2400 cm^{-1} is disappeared implying the complete substitution of carboxylic acid group to ester group, while the

hydroxyl group of phenol is confirmed at 3180 cm^{-1}. This implies the structure of **1**, which was also confirmed by the Aldrich library of FT-IR[13]. ^1H NMR clarifies the peaks at 1.36 and 4.33 belonging to methyl and methylene protons of ethyl group, respectively[14] (Figure 2).

To enhance the hydrophobicity of the molecules as proposed (scheme I), compounds **2-7** were prepared by varying the types of amine in Mannich reaction. For example, in the case of **2**, **4**, and **7** compounds obtained can be easily confirmed from the peak of oxazine ring at 1497 cm^{-1}(Figure 3). It has to note that there is some OH peak remained in 3000-2400 cm^{-1} which might be due to the trace of carboxylic acid left in **4**. ^1H NMR shows two singlet peaks at 3.9 and 4.8 ppm referring to methylene protons on the oxazine ring (Figure 4). The results insisted that compound **2** was successfully prepared.

Recently, Laobuthee et al.[13] reported that the ring opening reaction of *p*-substituted based benzoxazine terminated at dimer level, thus, the present work applied the reaction to accomplish **8-13** by using **2-7** react with **1** in stoichiometric ratio. Figure 5 confirms the successful of the reaction to give **8**, **10**, and **13** from C-N stretching at 1500 cm^{-1} and OH peak at 3400 cm^{-1} [11]. Figure 6 clarifies the existence of methylene linkage from peak at 3.98 ppm. It is important to note that the compound **8-13** show typical FTIR pattern with intermolecular H-bond at 3400 and intramolecular H-bond at 3300-2800 cm^{-1}. Laobuthee et al.[11] declared that the two types of H-bond are the main factor to generate the crystal packing unit of aza-methylene phenol with a simultaneous network.

Thermal Properties. By changing the structure of aza methylene phenol with an enhancement in hydrophobicity at aza group, it is expected that the molecular alignment might be induced depending on the chain packing. Thermal analysis was applied to observe the stability of the compounds. Recently, Hemvichian et al.[15] reported the degradation of polybenzoxazine by using aza methylene phenol as a model compound. The results observed by TGA and Mass spectroscopy analysis indicated that aza-methylene phenol gives the degradation for two steps. The first step is the bond cleavage of methylene linkage either at C-N or C-C bond at approximately 200°C. The C-N and C-C bond cleavage occurs at

relatively high temperature also implied the network of inter and intramolecular hydrogen bond as clarified by Laobuthee et al[11]. After that the recombination of the ring happened and the intermediate was restabilized to be biphenol compounds. The degradation at the second stage, thus, occurred at biphenol degradation temperature of 400-500°C.

Table 1 shows the degradation temperature (T_d) and melting temperature (T_m) observed by TGA and DSC, respectively. Compound **8** was used as a reference of backbone unit while **9-12** were applied to observe the effect of hydrophobic group to the backbone. In addition, **13** was an example for steric effect involved in the backbone of aza-methylene phenol. It is important to note that all compounds perform the degradation temperature in the same trend as reported by Hemvichian et al. This reflects that the hydrophobicity onto the aza group have little effect to the stability of the backbone of aza methylene phenol unit.

Compound **13** gives the lowest T_d and T_m. This might reflect the fact that the chair form of cyclohexyl group brings the steric effect to the chain packing. As a result, the relatively weak inter and intramolecular hydrogen bonds are formed as compared to other compounds.

Thermal responsive chain packing structure. Wide-angle x-ray diffraction with high temperature attachment system was applied to observe the change of packing structure as a function of temperature. In the case of **8**, which has the simple backbone molecule of aza-methylene phenol, the XRD patterns under various temperatures are constant until the melt starts (150°C) (Figure 7). In contrast, compounds **10** and **13**, the packing structures are drastically changed soon after the thermal condition was close to 90°C (Figures **8** and **9**). This implies that the hydrophobic group or the bulky group, which are cyclohexyl group and hexyl group, induces the thermal responsive packing structure. Sakurai et al.[16] reported the molecular assembly of dodecylbenzensulfonic acid and nicotinic acid complex, which was observed by WAXD. In our case, we speculated that the assembly structure might be formed not only by the hydrophobic interaction but also inter and intramolecular hydrogen bonds[11] (Figure 5). The movement of the aza group might induce the thermal responsive molecular alignment.

Conclusions

Aza-methylene phenol compounds with various aza groups were successfully prepared by using the ring opening reaction of benzoxazine pathway. The structural characterizations implied that compounds **8-13** have inter and intramolecular hydrogen bonding to stabilize the compound. Thermal stability studies indicated that the degradation of aza-methylene phenol was related to the aza-methylene phenol backbone while the functional group at aza group has little effect. Compounds **8**, **10**, and **13** were used for comparative studies in thermal responsive chain packing structure. The results from high temperature attachment WAXD system declared that the chain packing in the case of the compounds with cyclohexyl or hexyl group are responsive to the thermal condition while the one with methyl group is not.

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Figure Captions

Figure 1. FTIR spectra of: (a) 4-hydroxybenzoic acid, and (b) **1**.

Figure 2. ^{1}H NMR spectrum of **1**.

Figure 3. FTIR spectra of: (a) **2** (b) **4**, and (c) **7**.

Figure 4. ^{1}H NMR spectrum of **4**.

Figure 5. FTIR spectra of: (a) **8**, (b) **10**, and (c) **13**.

Figure 6. ^{1}H NMR spectrum of **10**.

Figure 7. XRD diffraction patterns of: **8** at (a) 30°C, (b) 60 °C, (c) 90 °C, (d) 120 °C, and (e) 150 °C.

Figure 8. XRD diffraction patterns of: **10** at (a) 30°C, (b) 60 °C, (c) 90 °C, (d) 120°C, and (e) 150 °C.

Figure 9. XRD diffraction patterns of: **13** at (a) 30°C, (b) 60 °C, (c) 90 °C, (d) 120°C, and (e) 150 °C.

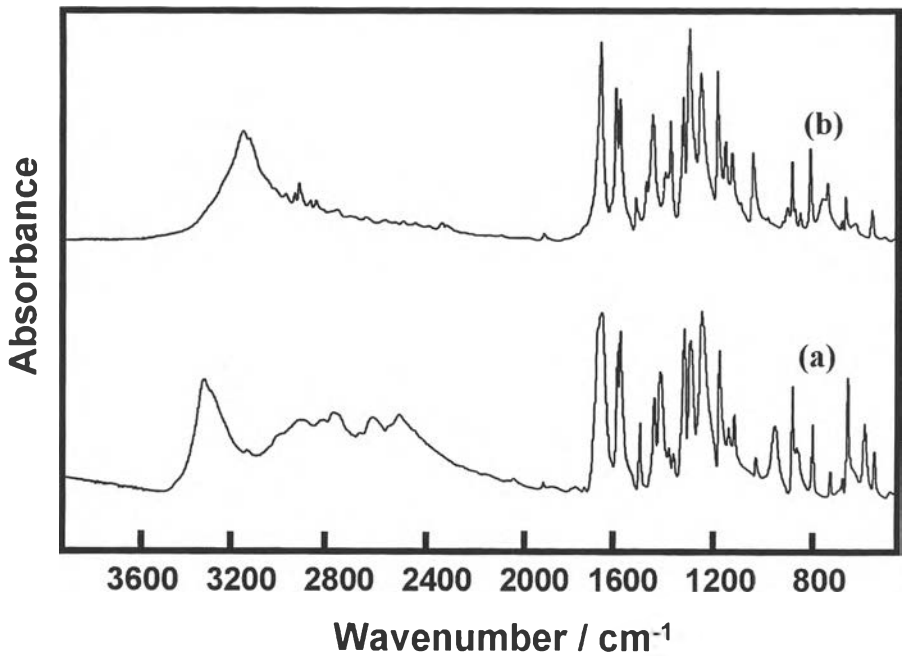


Figure 1. (Chanchai et al.)

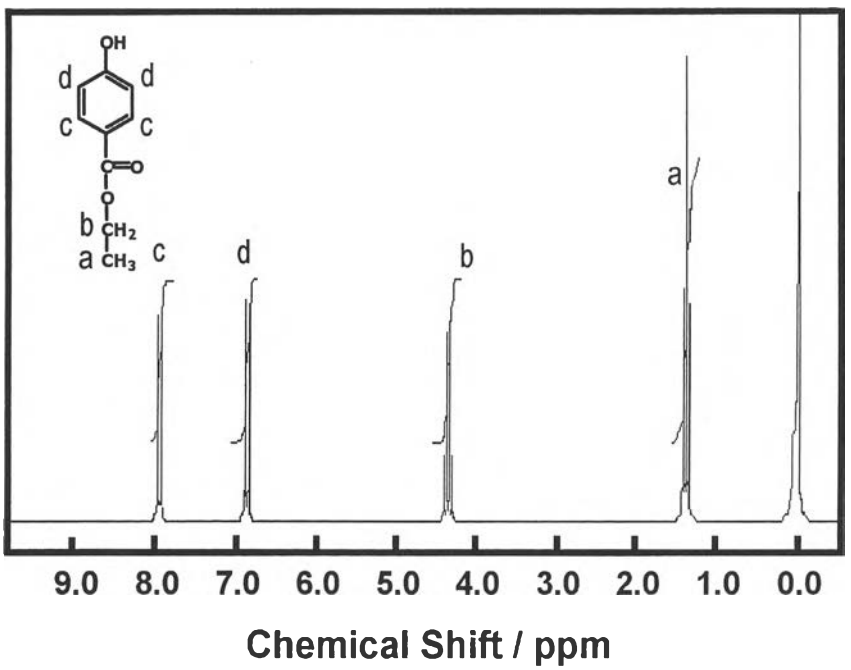


Figure 2. (Chanchai et al.)

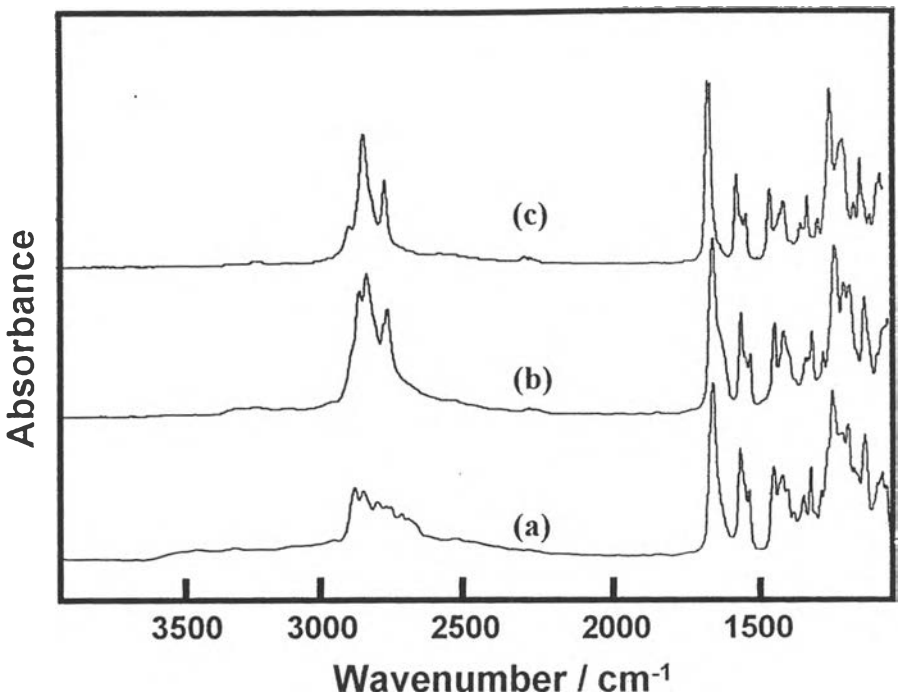


Figure 3. (Chanchai et al.)

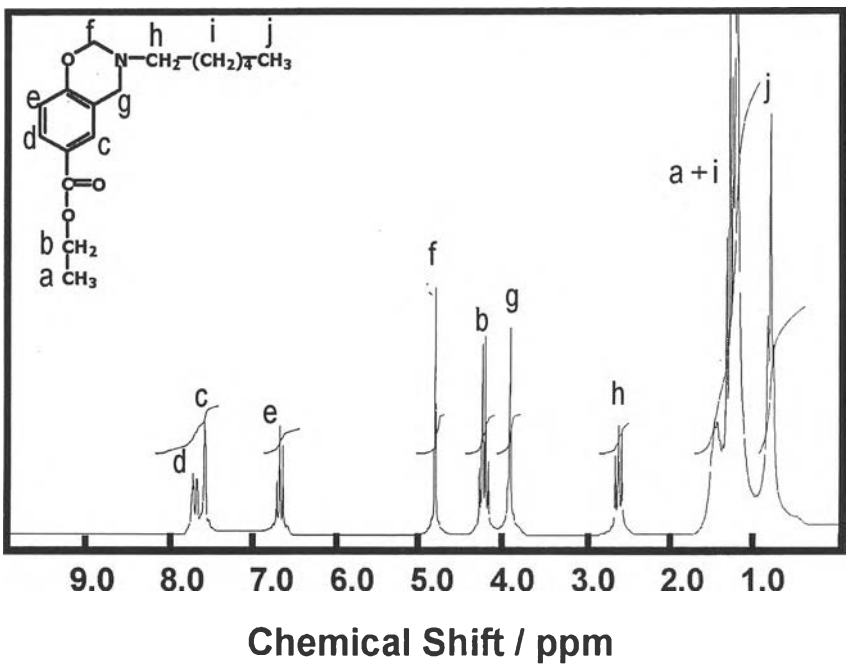


Figure 4. (Chanchai et al.)

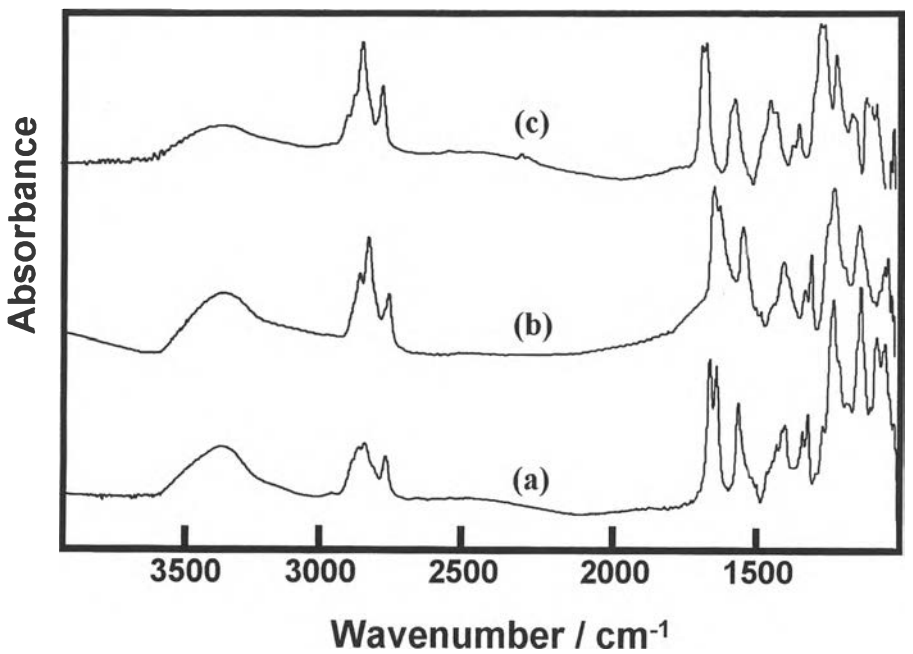


Figure 5. (Chanchai et al.)

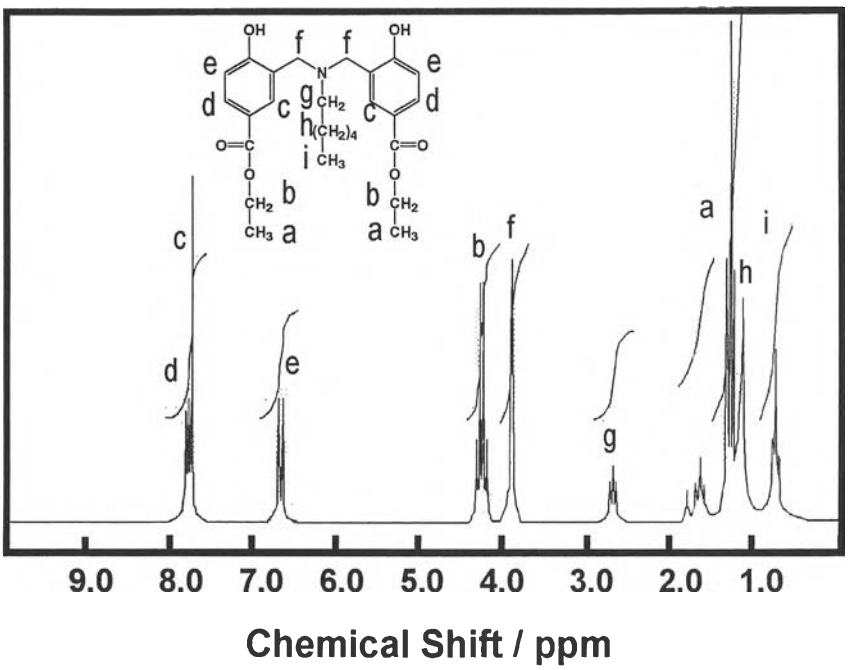


Figure 6. (Chanchai et al.)

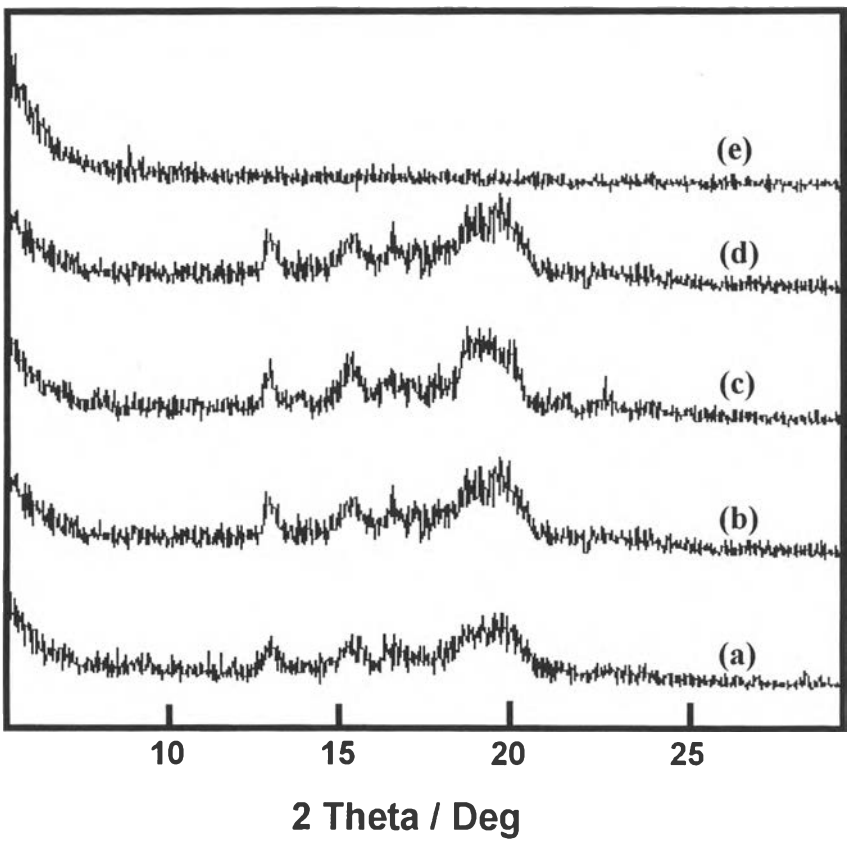


Figure 7. (Chanchai et al.)

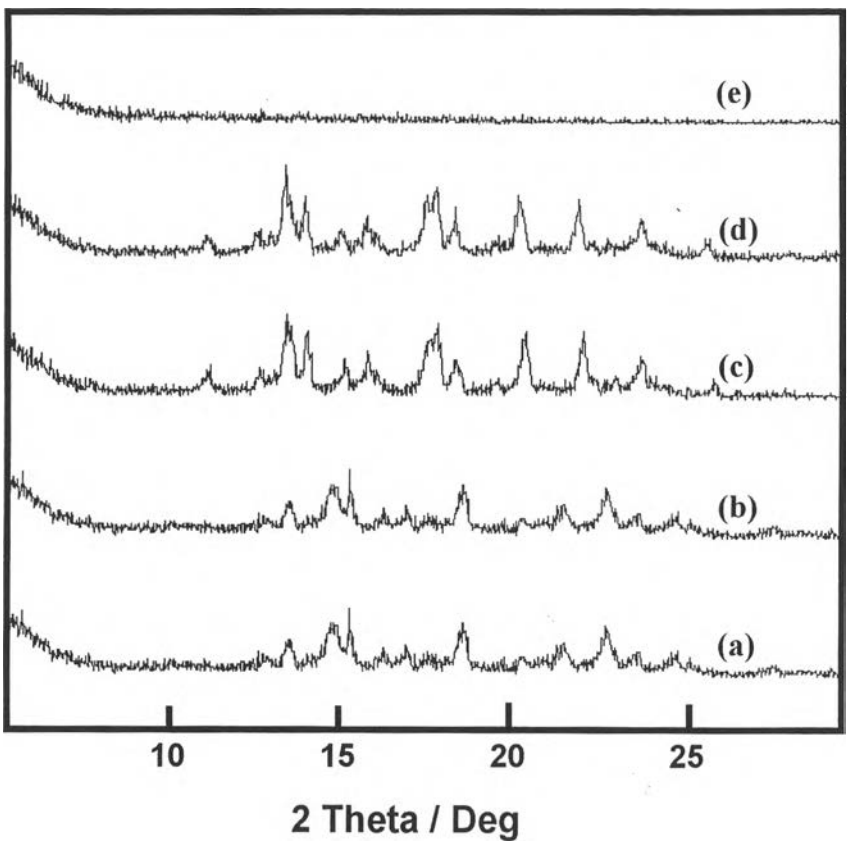


Figure 8. (Chanchai et al.)

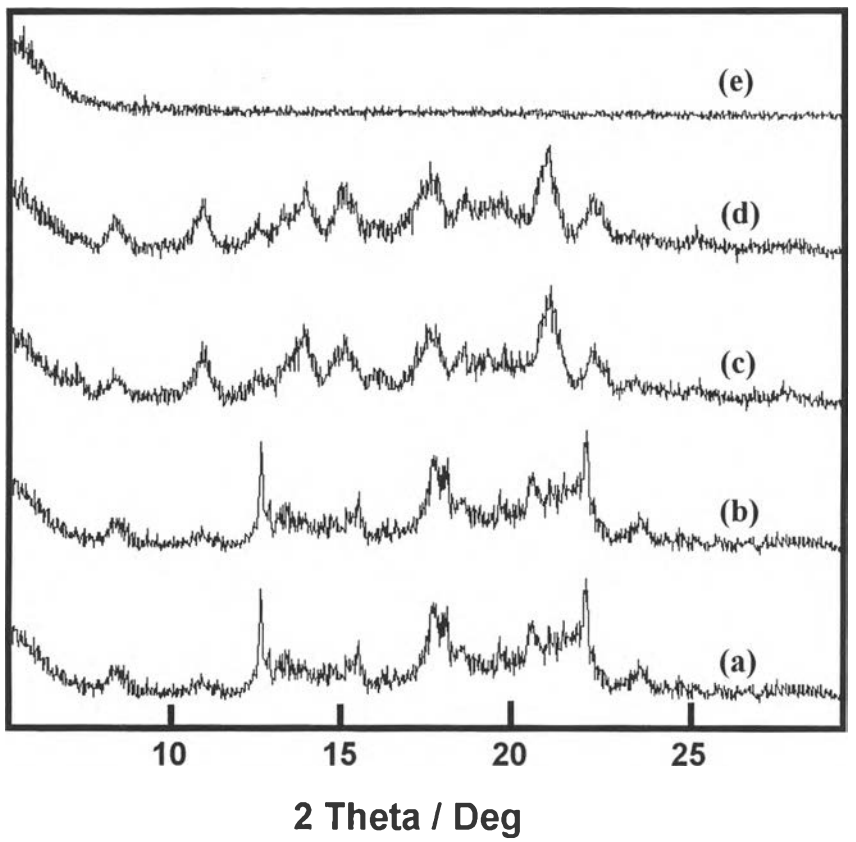


Figure 9. (Chanchai et al.)

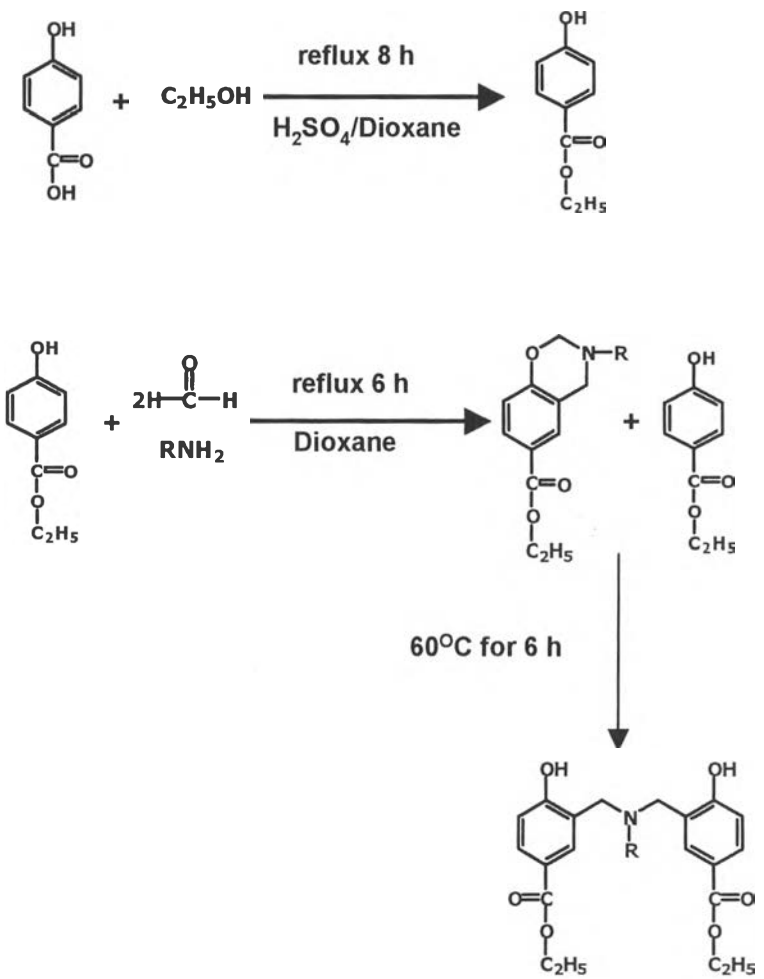
Table Caption

Table 1. Thermal stability of compounds **8-13**

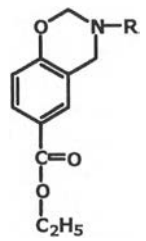
Compound	Degradation Temperature (T_d)/ °C	Melting Temperature (T_m)/ °C
8	205, 395	182
9	195,405	-
10	202, 394	182
11	199, 396	-
12	199,398	-
13	189,401	169

Table 1. (Chanchai et al.)

Scheme I


OH
C=O
OH
+
C2H5OH
reflux 8 h
H2SO4/Dioxane
OH
C=O
O
C2H5
OH
C=O
O
C2H5
+
2H—C—H
O
RNH2
reflux 6 h
Dioxane
O
N—R
C=O
O
C2H5
+
OH
C=O
O
C2H5
60°C for 6 h
OH
OH
N
R
O=C
C=O
O
C2H5
O
C2H5

Scheme II



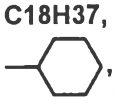
R = CH3, (2)

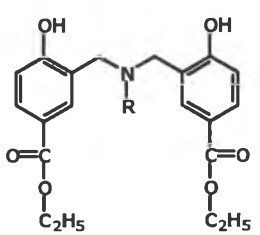
= C3H7, (3)

= C6H13, (4)

= C12H25, (5)

= C18H37, (6)

=  , (7)



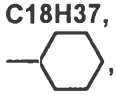
R = CH3, (8)

= C3H7, (9)

= C6H13, (10)

= C12H25, (11)

= C18H37, (12)

=  , (13)